ERRATUM NOTICE

General Certificate of Education
June 2007

CHEMISTRY **CHM4**
Unit 4 Further Physical and Organic Chemistry

Monday 18 June 2007 1.30 pm to 3.00 pm

Instructions to Invigilators

Before the start of the examination please ask candidates to amend their question papers as follows.
(Please read out this message twice to ensure understanding.)

Turn to page 16, question 8 (a) (iii)

The formula at the end of the line should read '$CH_3CH_2CONHCH_3$' so add 'CH_2' after the first CH_3. This makes the formula the same as Amide **R** in the first line of the stem of part (a).

Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

For Examiner's Use

General Certificate of Education
June 2007
Advanced Level Examination

CHEMISTRY **CHM4**
Unit 4 Further Physical and Organic Chemistry

Monday 18 June 2007 1.30 pm to 3.00 pm

For this paper you must have
- a calculator.

Time allowed: 1 hour 30 minutes

Instructions

- Use blue or black ink or ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- Answer the questions in **Section A** and **Section B** in the spaces provided.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.
- The Periodic Table/Data Sheet is provided on pages 3 and 4. Detach this perforated sheet at the start of the examination.
- **Section B** questions are provided on a perforated sheet. Detach this sheet at the start of the examination.

Information

- The maximum mark for this paper is 90.
- The marks for questions are shown in brackets.
- You are expected to use a calculator where appropriate.
- Write your answers to the question in **Section B** in continuous prose, where appropriate. You will be assessed on your ability to use an appropriate form and style of writing, to organise relevant information clearly and coherently, and to use specialist vocabulary, where appropriate.

Advice

- You are advised to spend about 1 hour on **Section A** and about 30 minutes on **Section B**.

For Examiner's Use			
Question	Mark	Question	Mark
1			
2			
3			
4			
5			
6			
7			
8			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

LEAVE MARGIN BLANK

SECTION A

Answer **all** questions in the spaces provided.

1 When sulphur dioxide and oxygen are mixed in a closed container and heated in the presence of a catalyst, the following equilibrium is established.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^\ominus = -196 \text{ kJ mol}^{-1}$$

An expression for the equilibrium constant, K_p, for this reaction is shown below.

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 (p_{O_2})}$$

(a) (i) Deduce the units of K_p when pressures are measured in kPa.

....

(ii) In an equilibrium mixture established at temperature T_1, the partial pressure of sulphur dioxide is 10.6 kPa and the partial pressure of sulphur trioxide is 90.8 kPa. Calculate the partial pressure of oxygen in this mixture, given that the value of K_p for the equilibrium at temperature T_1 is 1.42

....

....

....

....

(4 marks)

(b) A mixture of sulphur dioxide, oxygen and sulphur trioxide has reached equilibrium in a closed container at temperature T_1.

(i) State and explain the effect, if any, on the mole fraction of sulphur trioxide in the equilibrium mixture if the volume of the container is decreased at constant temperature.

Effect on mole fraction of sulphur trioxide ....

Explanation ....

....

(ii) State the effect, if any, on the value of K_p if the volume of the container is decreased at constant temperature.

....

The Periodic Table of the Elements

■ The atomic numbers and approximate relative atomic masses shown in the table are for use in the examination unless stated otherwise in an individual question.

Key

relative atomic mass — 6.9 **Li** Lithium — atomic number 3

I	II											III	IV	V	VI	VII	0
1.0 **H** Hydrogen 1																	4.0 **He** Helium 2
6.9 **Li** Lithium 3	9.0 **Be** Beryllium 4											10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12											27.0 **Al** Aluminium 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulphur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	45.0 **Sc** Scandium 21	47.9 **Ti** Titanium 22	50.9 **V** Vanadium 23	52.0 **Cr** Chromium 24	54.9 **Mn** Manganese 25	55.8 **Fe** Iron 26	58.9 **Co** Cobalt 27	58.7 **Ni** Nickel 28	63.5 **Cu** Copper 29	65.4 **Zn** Zinc 30	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	88.9 **Y** Yttrium 39	91.2 **Zr** Zirconium 40	92.9 **Nb** Niobium 41	95.9 **Mo** Molybdenum 42	98.9 **Tc** Technetium 43	101.1 **Ru** Ruthenium 44	102.9 **Rh** Rhodium 45	106.4 **Pd** Palladium 46	107.9 **Ag** Silver 47	112.4 **Cd** Cadmium 48	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Caesium 55	137.3 **Ba** Barium 56	138.9 **La** Lanthanum 57 *	178.5 **Hf** Hafnium 72	180.9 **Ta** Tantalum 73	183.9 **W** Tungsten 74	186.2 **Re** Rhenium 75	190.2 **Os** Osmium 76	192.2 **Ir** Iridium 77	195.1 **Pt** Platinum 78	197.0 **Au** Gold 79	200.6 **Hg** Mercury 80	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	210.0 **Po** Polonium 84	210.0 **At** Astatine 85	222.0 **Rn** Radon 86
223.0 **Fr** Francium 87	226.0 **Ra** Radium 88	227 **Ac** Actinium 89 †															

* **58 – 71** Lanthanides	140.1 **Ce** Cerium 58	140.9 **Pr** Praseodymium 59	144.2 **Nd** Neodymium 60	144.9 **Pm** Promethium 61	150.4 **Sm** Samarium 62	152.0 **Eu** Europium 63	157.3 **Gd** Gadolinium 64	158.9 **Tb** Terbium 65	162.5 **Dy** Dysprosium 66	164.9 **Ho** Holmium 67	167.3 **Er** Erbium 68	168.9 **Tm** Thulium 69	173.0 **Yb** Ytterbium 70	175.0 **Lu** Lutetium 71
† **90 – 103** Actinides	232.0 **Th** Thorium 90	231.0 **Pa** Protactinium 91	238.0 **U** Uranium 92	237.0 **Np** Neptunium 93	239.1 **Pu** Plutonium 94	243.1 **Am** Americium 95	247.1 **Cm** Curium 96	247.1 **Bk** Berkelium 97	252.1 **Cf** Californium 98	(252) **Es** Einsteinium 99	(257) **Fm** Fermium 100	(258) **Md** Mendelevium 101	(259) **No** Nobelium 102	(260) **Lr** Lawrencium 103

Gas constant $R = 8.31$ J K^{-1} mol^{-1}

Table 1
Proton n.m.r chemical shift data

Type of proton	δ/ppm
RCH_3	0.7–1.2
R_2CH_2	1.2–1.4
R_3CH	1.4–1.6
$RCOCH_3$	2.1–2.6
$ROCH_3$	3.1–3.9
$RCOOCH_3$	3.7–4.1
ROH	0.5–5.0

Table 2
Infra-red absorption data

Bond	Wavenumber/cm^{-1}
C—H	2850–3300
C—C	750–1100
C=C	1620–1680
C=O	1680–1750
C—O	1000–1300
O—H (alcohols)	3230–3550
O—H (acids)	2500–3000

(iii) When the temperature of the equilibrium mixture is changed from T_1 to T_2 at constant volume, the partial pressure of sulphur trioxide decreases. Deduce which temperature, T_1 or T_2, is the higher. Explain your answer.

Higher temperature ....

Explanation ....

....

(5 marks)

(c) A different equilibrium mixture of these three gases is prepared at temperature T_1 and total pressure P. In this mixture, the mole fraction of sulphur trioxide is 0.75 and the mole fraction of sulphur dioxide is 0.17

(i) Calculate the mole fraction of oxygen in this mixture.

....

(ii) Write an expression which relates the partial pressure of a gas to its mole fraction and the total pressure P.

....

(iii) Use your answer to part (c)(ii) and the value of K_p given in part (a)(ii) to calculate a value for the total pressure P.

....

....

....

....

....

....

(5 marks)

14

2 (a) (i) Write an expression for the term pH.

....

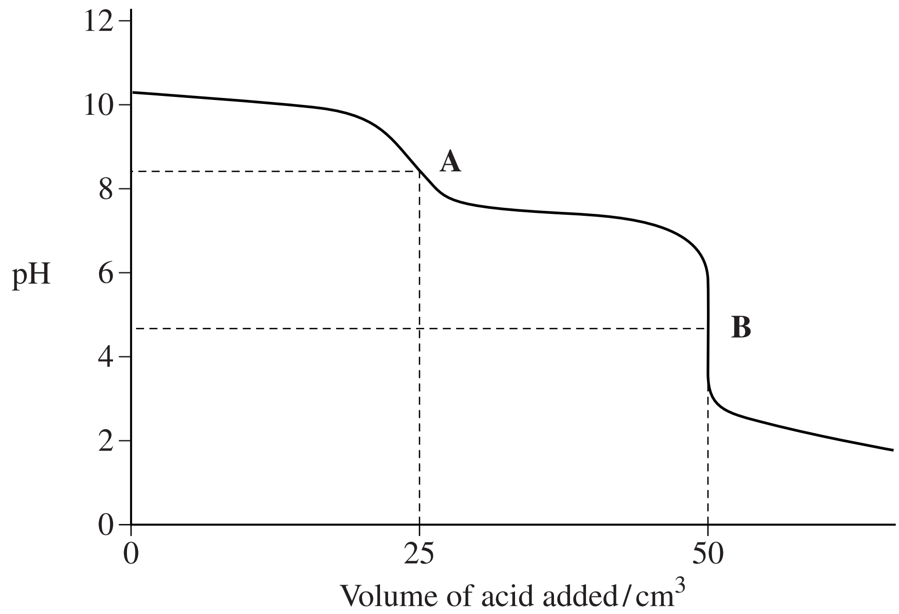
(ii) Calculate the concentration of hydrochloric acid which has a pH value of 0.36

....

....

(2 marks)

(b) The curve below shows how the pH changes when hydrochloric acid is added to an aqueous solution of sodium carbonate.



(i) Write an equation for the reaction which occurs before equivalence point **A** and an equation for the reaction which occurs between equivalence points **A** and **B**.

Equation for reaction before ***A***

....

Equation for reaction between ***A*** *and* ***B***

....

(ii) A list of indicators is shown in the table below.

Indicator	**pH range**
trapaeolin	1.3 – 3.0
bromophenol blue	3.0 – 4.6
phenol red	6.8 – 8.4
metacresol purple	7.6 – 9.2
thymolphthalein	9.3 – 10.5
nitramine	10.8 – 13.0

Select from the list the best indicator for the equivalence point **A** and, in a separate experiment, the best indicator for the equivalence point **B**.

*Indicator for equivalence point **A*** ....

*Indicator for equivalence point **B*** ....

(iii) This pH curve was obtained when a 40.0 cm^3 sample of 0.150 $mol\,dm^{-3}$ aqueous sodium carbonate was used. Calculate the number of moles of sodium carbonate in this sample.

....

....

(iv) Use the volume of hydrochloric acid which has been added at the equivalence point **B** to calculate the concentration of the hydrochloric acid used.

....

....

....

....

(7 marks)

9

Turn over ▶

LEAVE MARGIN BLANK

3 When answering this question, assume that the temperature is 298 K and give all pH values to 2 decimal places.

The acid dissociation constant, K_a, of propanoic acid, CH_3CH_2COOH, has the value 1.35×10^{-5} mol dm^{-3}.

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

(a) Calculate the pH of a 0.550 mol dm^{-3} solution of propanoic acid.

....

....

....

....

....

(3 marks)

(b) A buffer solution is formed when 10.0 cm^3 of 0.230 mol dm^{-3} aqueous sodium hydroxide are added to 30.0 cm^3 of 0.550 mol dm^{-3} aqueous propanoic acid.

(i) Calculate the number of moles of propanoic acid originally present.

....

(ii) Calculate the number of moles of sodium hydroxide added.

....

(iii) Hence, calculate the number of moles of propanoic acid present in the buffer solution.

....

(iv) Hence, calculate the pH of the buffer solution.

....

....

....

....

....

....

(6 marks)

9

LEAVE MARGIN BLANK

4 (a) The rate equation for the reaction between compounds **C** and **D** is

$$\text{rate} = k[\mathbf{C}][\mathbf{D}]^2$$

(i) In an experiment where the initial concentration of **C** is 0.15 mol dm^{-3} and the initial concentration of **D** is 0.24 mol dm^{-3}, the initial rate of reaction is 0.65 mol dm^{-3} s^{-1} at a given temperature. Calculate a value for the rate constant, *k*, at this temperature and deduce its units.

Value of k ....

....

....

Units of k ....

....

(ii) The reaction between **C** and **D** is repeated in a second experiment at the same temperature, but the concentrations of both **C** and **D** are half of those in part (a)(i). Calculate the initial rate of reaction in this second experiment.

....

....

(4 marks)

(b) The following data were obtained in a series of experiments on the rate of the reaction between compounds **E** and **F** at a constant temperature.

Experiment	Initial concentration of **E** / mol dm^{-3}	Initial concentration of **F** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.24	0.64	0.80×10^{-2}
2	0.36	0.64	1.80×10^{-2}
3	0.48	0.32	3.20×10^{-2}

(i) Deduce the order of reaction with respect to **E**.

....

....

(ii) Deduce the order of reaction with respect to **F**.

....

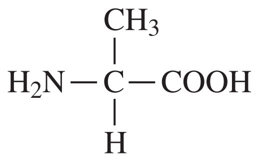
....

(2 marks)

6

Turn over ▶

5 (a) The structure of the amino acid *alanine* is shown below.



(i) Draw the structure of the zwitterion formed by *alanine*.

(ii) Draw the structure of the organic product formed in each case from *alanine* when it reacts with:

CH_3OH in the presence of a small amount of concentrated sulphuric acid

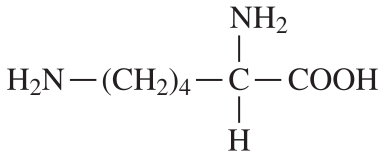
Na_2CO_3

CH_3Cl in a 1:1 mole ratio

(4 marks)

LEAVE MARGIN BLANK

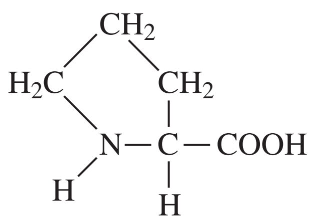
(b) The amino acid *lysine* is shown below.



Draw the structure of the *lysine* species present in a solution at low pH.

(1 mark)

(c) The amino acid *proline* is shown below.



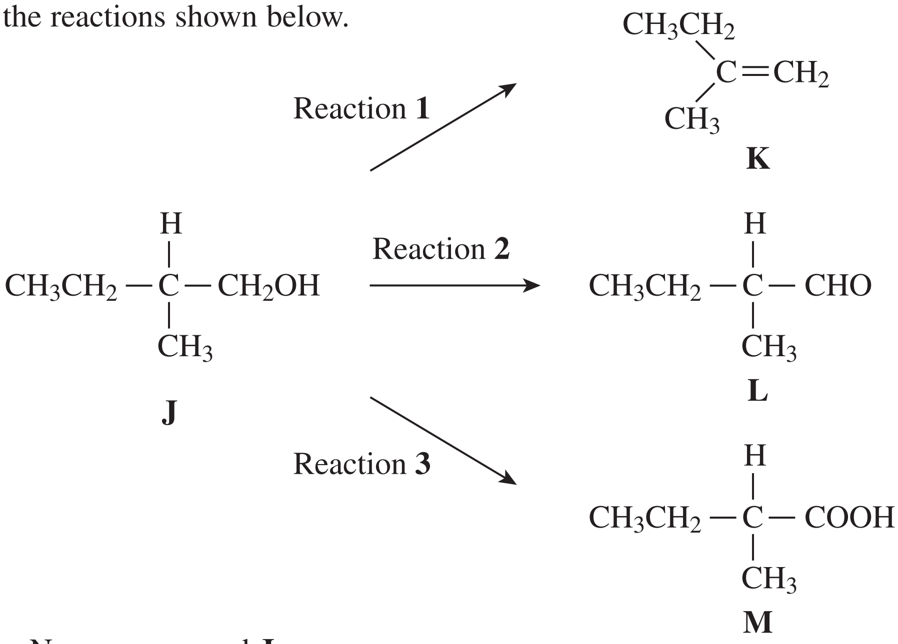
Draw the structure of the dipeptide formed from two *proline* molecules.

(1 mark)

6

Turn over ▶

6 Consider the reactions shown below.



(a) (i) Name compound **J**

....

(ii) Compound **J** exists as a pair of stereoisomers. Name this type of stereoisomerism.

....

(2 marks)

(b) (i) Name the type of mechanism for Reaction **1**.

....

(ii) Draw the repeating unit of the polymer formed by **K** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation ....

(iii) Draw the structure of an isomer of **K** which shows stereoisomerism.

(iv) Draw the structure of an isomer of **K** which has only one peak in its proton n.m.r. spectrum.

(5 marks)

(c) (i) Draw the structure of an isomer of **L** which has no effect on either Fehling's or Tollens' reagents and has only two peaks in its proton n.m.r. spectrum.

(ii) Acidified potassium dichromate(VI) reacts with **J** to form both **L** and **M**. What practical technique is used to obtain **M** rather than **L**?

....

(2 marks)

(d) The four infra-red spectra **I**, **II**, **III** and **IV** shown on the perforated page 15 are those of compounds **J**, **K**, **L** and **M**, but not necessarily in that order. Using **Table 2** on the data sheet, page 4, give the letter corresponding to the correct compound for each spectrum.

Spectrum **I** ....

Spectrum **II** ....

Spectrum **III** ....

Spectrum **IV** ....

(4 marks)

(e) (i) Give an approximate range of wavenumbers for the fingerprint region in an infra-red spectrum.

....

(ii) Describe how the fingerprint region can be used to identify a compound.

....

....

....

(3 marks)

16

Section B, Questions 7 and 8 are printed on page 16, the reverse of the spectra.

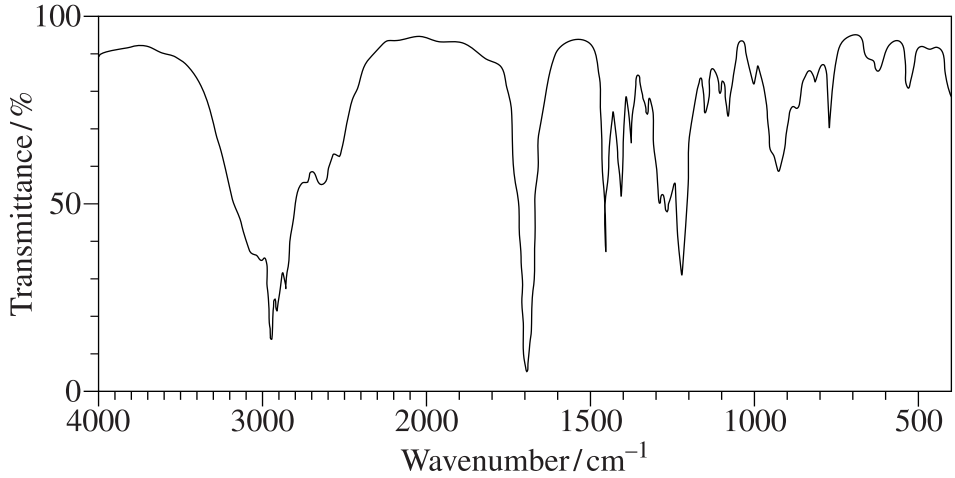
Answer these questions in the space provided on pages 14 and 17 to 20 of this booklet.

Turn over ►

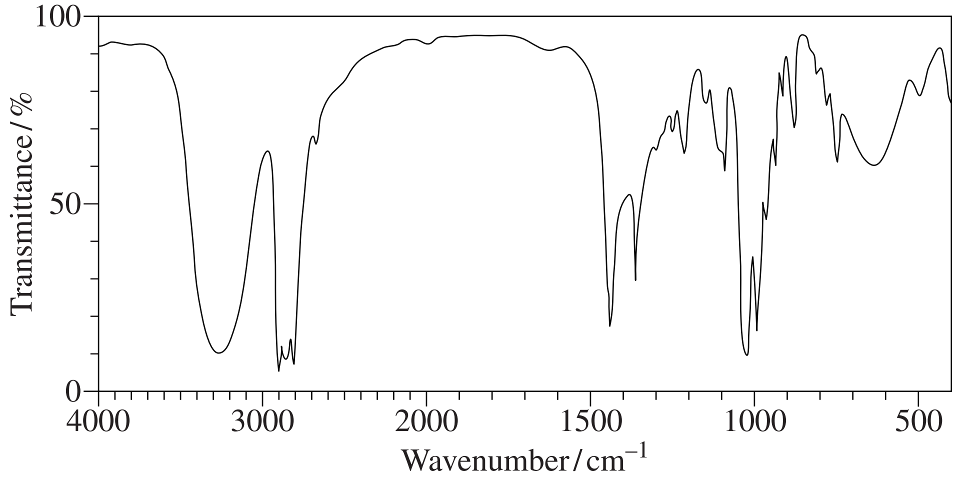
LEAVE MARGIN BLANK

The infra-red spectra below are for use with Question 6 on pages 12 and 13.

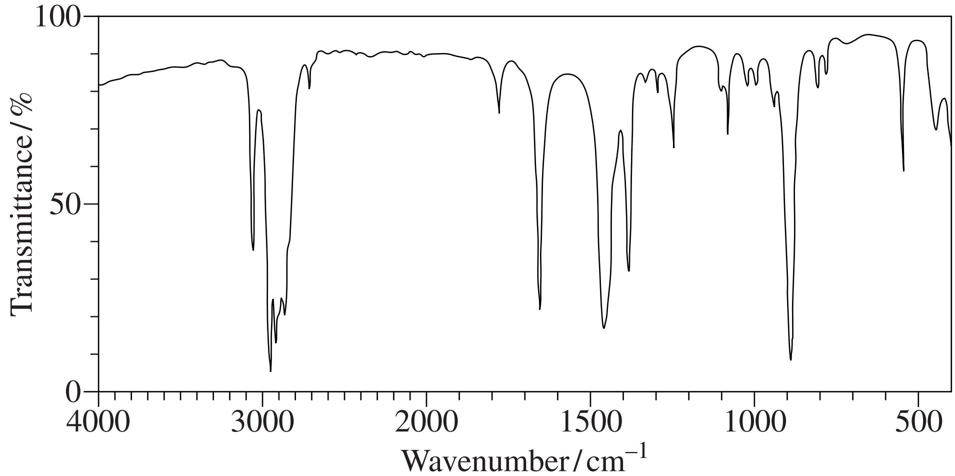
I



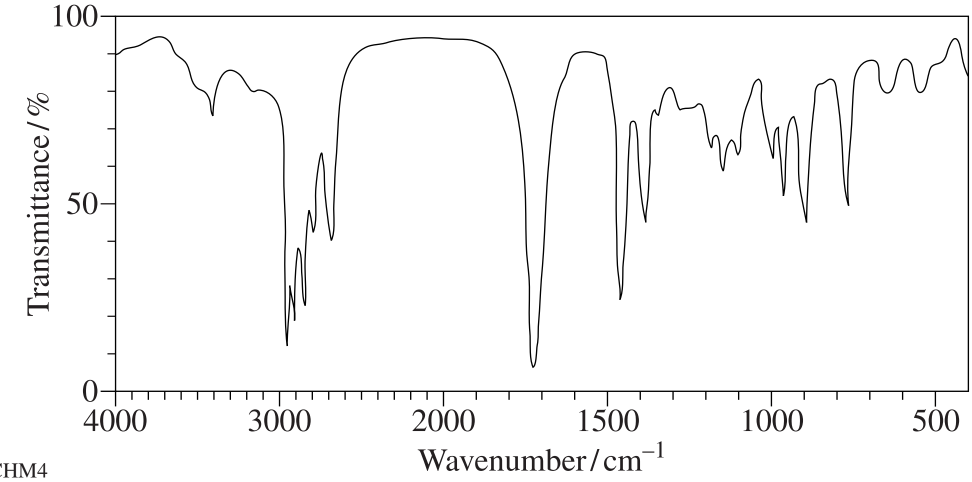
II



III



IV



Turn over ▶

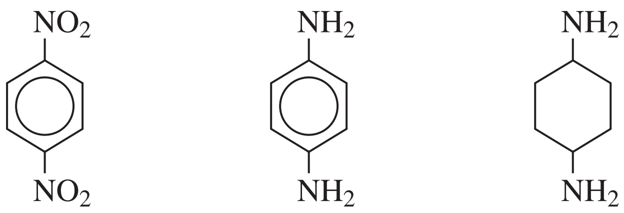
SECTION B

Answer **both** questions in the space provided on pages 14 and 17 to 20 of this booklet.

7 (a) Give reagents and conditions and write equations to show the formation of nitrobenzene from benzene.
Name and outline a mechanism for this reaction of benzene.

(8 marks)

(b) Compounds **X**, **Y** and **Z** are shown below.



X **Y** **Z**

Name **X** and give reagents for the conversion of **X** into **Y**. Write an equation for this reaction using [H] to represent the reductant.
Explain why **Y** is a weaker base than **Z**.

(6 marks)

(c) Draw the repeating unit of the polymer formed by the reaction of **Y** with hexanedioic acid.

(2 marks)

8 (a) Amide **R**, $CH_3CH_2CONHCH_3$, can be formed by the reaction of CH_3CH_2COCl with CH_3NH_2

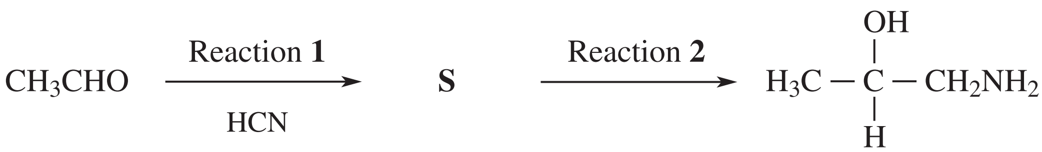
(i) Name amide **R**. Name and outline a mechanism for the reaction of CH_3CH_2COCl with CH_3NH_2 to form **R**.

(ii) **R** can also be formed by the reaction of an acid anhydride with CH_3NH_2
Draw the structure of this acid anhydride.

(iii) In the mass spectrometer, fragmentation of the molecular ion of $CH_3CONHCH_3$ produces a peak with *m/z* = 57. Write an equation for this fragmentation.

(10 marks)

(b) Consider the following reaction sequence.



Name the mechanism for Reaction **1** and deduce the structure of compound **S**.

Give the reagents and name the type of reaction occurring in Reaction **2**.

(4 marks)

END OF QUESTIONS

LEAVE
MARGIN
BLANK

Turn over ▶

LEAVE MARGIN BLANK

LEAVE
MARGIN
BLANK

LEAVE MARGIN BLANK